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STUDIES OF TUNGSTEN COMPOSITES CONTAINING FIBERED OR REACTED ADDITIVES

by Max Quatinetz, John W. Weeton, and Thomas P. Herbell

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SUMMARY

    Twenty-one sintered tungsten and tungsten-plus-additive billets were pre-
pared in order to evaluate the feasibility of producing fiber-bearing composites
by the elongation of materials in situ (in a tungsten matrix) during extrusion
and to study reactions between the additives and the matrix with the objective
of producing high-strength materials. Eight compounds, including oxides,
borides, nitrides, and carbides, ranging in melting point from 4370° to 7030° F
were successfully elongated in tungsten by extrusion at 4200° F. All composites
with less than 10-volume-percent additive exhibited improvements in stress-
rupture strength. Composites with highly elongated additives ranged from
4 to 18 times better in stress-rupture life at 3000° F than the unreinforced
pure tungsten matrix. The stress-rupture lives of several composites with more
reactive additives and only moderate fibering increased to 25 to 50 times that
of tungsten at 3000° F. The strengthening was presumed to be caused by re-
actions between the additives and the matrix. No judgment could be made from
the study as to what extent the in situ fibering contributed to the increased
strength. Because of inherent advantages, the in situ fibering method appears
to have great potential for producing strong fibered composite materials and
for producing fibers from strong, hard, and brittle refractory compounds and
other relatively nondeformable materials.

INTRODUCTION

    Progress in the space age depends greatly on the development of materials,
particularly those with high-temperature strength. Since tungsten has the
highest melting point of the metals, metallurgists anticipated that it would
prove to be the answer to many current needs and fill the requirements for a
large number of pressing space problems involving high temperatures. Tungsten,
however, has several deficiencies that limit its application. Besides its high
density and high ductile-to-brittle transition temperature, the strength prop-
erties of tungsten deteriorate rapidly with temperature in the temperature
range of interest. Considerable effort is currently being expended to improve
the high-temperature strength and stability of tungsten by the addition of
alloying elements and dispersoids.

From the standpoint of obtaining high-temperature strength, the greatest improvements have been achieved to date in the alloy field. In fact, minor alloying additives may significantly improve the elevated temperature properties of tungsten-base alloys. Some of the better alloys have included tungsten with small additions of columbium or tantalum with or without carbon (ref. 1).

In the area of strengthening by dispersoid additions (particularly oxides), one of the better systems has been tungsten and thoria. Recently obtained properties of such materials are given in reference 1. Even in the case of the alloys strengthened by solid-solution additions, it is believed that a good portion of their strength may be attributed to the formation of dispersoids resulting from combinations of reactive alloying additives with interstitials (ref. 2). From the standpoint of thermodynamics, oxides should be more stable than refractory compounds (carbides, nitrides, and borides). In spite of the differences in the thermodynamic stability of the materials, refractory compounds in tungsten materials have been as strong at elevated temperatures as materials containing oxides (ref. 3). Because tungsten must be processed at relatively high temperatures, reactions are more likely to take place between the additive and the matrix than in matrices, which are processed at lower temperatures.

Another possible mechanism by which tungsten could be strengthened is the addition of fibers. At the Lewis Research Center it was shown that tungsten fibers in a copper matrix carry a load proportional to the volume percent of fibers in the composite (ref. 4). In fact, it was shown that each constituent in the composite carried its full share of the load. Similarly, ceramic fiber composites in the form of aluminum oxide whiskers embedded in a silver matrix by Sutton, Chorné, and Gatti (ref. 5) also exhibited an increasing strength with increasing volume percent of fibers.

Most of the work that has been done in the fiber-reinforcement field has involved the incorporation of high-melting-point fibers in low-melting-point matrices; thus, the literature does not furnish much background information for studies on higher melting point materials. A number of inherent difficulties are involved in the fiber reinforcement of refractory materials. With low-melting composites, the melting point of the additive is generally well above that of the matrix, while with refractory matrices, there are fewer additives with suitable melting points, and these high-temperature materials have not been readily available in fiber form. Also, there is more possibility of damage to the fiber during the processing necessary to embed the fiber in the matrix at higher temperatures. Finally, as in the case of dispersion strengthening of refractory matrices, it would be necessary to have fiber additives that would be thermodynamically stable and would not tend to react with the matrix or other elements present (impurities or interstitials, etc.) at the high processing and use temperatures employed. Nevertheless, with strong, stable materials, fibers should be capable of strengthening high-temperature matrices in a manner similar to that in which they strengthen low-melting systems.

Earlier work at the Lewis Research Center to extend the extrusion capabilities of refractory materials indicated that some highly refractory oxides

could be elongated by the extrusion process. The elongation of low-melting materials in low-melting matrices, such as silicate slags in steel and in wrought iron, as well as inorganic compounds in free machining steels and in nonferrous alloys, has been observed in the microstructures of these materials. By analogy it seemed reasonable that deliberate fibering of refractory additives could be accomplished in situ (in a high-melting-point matrix) by extrusion at high temperature. If successful, the in situ method could overcome two major obstacles to fiber reinforcing of high-melting materials, namely, the lack of suitable fibers and the possibility of damage to the fibers during high-temperature processing. By this approach equiaxed additives could be embedded in a matrix and then elongated into fibers by extrusion. Thus, the fibers would be created and embedded more or less simultaneously during the processing. In order to explore the feasibility and significance of the in situ approach in the fiber-metallurgy field and to obtain information with regard to the stability of refractory additives in refractory matrices that could be applied to dispersion strengthening as well, it was decided to make refractory composites starting with relatively coarse refractory additive powders having a wide range of melting temperatures and reactivity. The objective of the investigation was to determine how effectively high-melting additives, oxides and refractory compounds, could be elongated in situ in high-melting matrices (in this case tungsten) by extrusion at high temperature and to observe the extent of reaction between the additives and the matrix. Also, it was intended to examine and determine various properties of the composites and to see if these could be related to the microstructures.

Composites consisting of a tungsten matrix with 5 to 26 volume percent of oxide or refactory compound were successfully extruded into bar stock. Four oxides, zirconia, yttria, hafnia, and thoria, and four refractory compounds, hafnium boride, nitride, and carbide and tantalum carbide, were used as additives. The billets were extruded at temperatures of 3700° to 4200° F at reduction ratios from 8:1 to 20:1. Stress-rupture tests of the extruded materials were conducted at temperatures of 2500° to 3800° F in vacuum. In addition, measurements of fiber length-diameter ratios, density, hardness, and grain size and metallographic studies of the composites were made.

MATERIALS AND PROCEDURES

A summary of materials, compositions, and processing techniques used with 21 compacted, sintered, and extruded tungsten and tungsten-plus-additive billets is given in tables I and II.

Billet Preparation

Raw materials. - The powders used in preparing the billets are listed in table I. All but one of the billets were made by using 2500 to 4000 grams of nominally 1-micron tungsten powder. The oxides zirconia, yttria, hafnia, and thoria were nominally 2 microns in average diameter as determined on a Fisher Sub-Sieve sizer. The refractory compounds hafnium boride, hafnium nitride, hafnium carbide, and tantulum carbide were nominally 4 to 7 microns in Fisher

TABLE I. - BILLET MATERIALS

Material	Source	Nominal purity, weight percent	Particle size, μ	Melting point, °F	Density, g/cc
Tungsten	General Electric Company	99.96	1.2	6170	19.30
Tungsten - 5 volume percent hafnia	Curtiss-Wright Corporation	99.74	2.0	----	----
Zirconia	Titanium Alloy Manufacturing Company	98.80	2.0	4892	5.49
Yttria	General Electric Company	-----	1.7	4370	4.84
Hafnia	Wah Chang Corporation	99.92	1.9	5090	9.68
Thoria	Lindsay Light and Chemical Company	-----	2.1	5522	10.03
Hafnium boride	The Carborundum Company	[a]93.3	6.8	5880	11.20
Hafnium nitride	The Carborundum Company	[b]96.6	4.6	5990	14.00
Hafnium carbide	The Carborundum Company	[c]95.4	4.2	7030	12.70
Tantalum carbide	Unknown	99.85	5.0	7020	14.65

[a]2.9 Percent zirconium, titanium, and carbon.

[b]3.0 Percent zirconium.

[c]4.6 Percent zirconium, titanium, and boron.

particle size. One billet was prepared with a tungsten powder obtained from Curtiss-Wright that already had 5 volume percent of hafnium oxide dispersed in it by the Triffleman process (ref. 6).

Mixing. - The powders used to prepare composites were weighed and added to a 2-quart jar filled approximately one-third full with 1/4-inch-diameter glass beads. Mixing occurred as the jars were rolled at relatively slow speeds, 30 to 60 rpm, for 24 hours. The speed was set so that the powder rolled gently over itself without sliding or clinging to the sides of the jar.

Cleaning. - In a number of cases (billets 2 to 5, table II) the tungsten and tungsten-additive mixtures were cleaned in a tower with a stream of hydrogen at 1500° F for 6 hours before compaction in order to reduce any tungsten oxide present to the metal. The hydrogen flow rate was set between 5 and 15 cubic feet per hour. The cleaning reaction was monitored with a phosphorous pentoxide electrochemical moisture meter. The cleaning tower was heated slowly in order to keep the moisture evolved below 1000 parts per million and to prevent localized sintering.

Compaction. - All the powders were compacted isostatically at 30 000 pounds per square inch and room temperature. The powder was packed initially in a rubber mold set in a $3\frac{3}{8}$-inch-inside-diameter metal tube so that, after pressing and sintering, the billet required a minimum of machining for canning and extruding in nominally 2-inch extrusion hardware.

Sintering. - Two different sintering schedules were used (table II). Billets 1 to 7 were sintered for 4 hours at a pressure of less than 5×10^{-5} torr and at temperatures from 3500° to 4200° F. In subsequent experiments, in order to obtain better density, the compacts were given a 2-hour presintering in hydrogen at 2600° F followed by a 2-hour sintering in vacuum at 4200° F.

TABLE II. - TUNGSTEN BILLET COMPOSITION AND PROCESSING

Billet	Composition Additive (b)	Amount of additive, volume percent	Extrusion[a] Temperature, °F	Reduction ratio	Can material	Can thickness, in.	Transfer time, sec	Maximum extrusion pressure, lb/sq in.	Ram speed, in./sec
Vacuum-sintered billets									
[c]1	--------	0	3700	8:1	Tantalum (sheet)	0.090	5	194.0×10³	6.0
[c,d]2	--------	0	4050				-	-----	4.0
[c,d]3	Zirconia	8.0	4200				5	183.0	5.3
[c,d]4	Yttria	8.0	4200				-	106.2	10.0
[c,d]5	Hafnia	10.0	4200				6	106.0	10.0
[e]6	Zirconia	5.0	3800	20:1	--------	-----	-	-----	----
[e]7	Zirconia	5.0	3800	20:1	--------	-----	-	-----	----
Hydrogen-presintered billets[f]									
8	--------	0	4200	8:1	Molybdenum (sintered powder)	0.250	5	115.7×10³	8.6
9	--------	0		16:1	Molybdenum (sintered powder)		5	-----	---
10	--------	0		16:1	Tantalum (sheet)		-	-----	---
11	Zirconia	14.5		8:1	Molybdenum (sintered powder)		8	79.8	14.4
12	Zirconia	20.5					5	96.8	4.8
13	Yttria	20.5					6	111.8	4.4
14	Hafnia	25.5					4.5	75.8	5.0
[g]15	Hafnia	23.5					6	151.7	4.0
16	Thoria	8.0					4.5	89.8	4.0
17	Thoria	16.0					15	125.7	3.6
18	Hafnium boride	8.0					5	131.7	9.8
19	Hafnium nitride	8.0					5	172.6	6.6
20	Hafnium carbide	8.0					4	197.6	4.0
21	Tantalum carbide	8.0					4	173.6	9.0

[a]Billets 6 and 7 extruded in high-energy press; all others extruded in a 1000-ton conventional press.

[b]All additives mixed 24 hr with glass beads in a jar on a ball mill; isostatically pressed at 30 000 psi.

[c]Sintered in vacuum at 3500° F for 2 hr and at 4200° F for 2 hr.

[d]Powder heated in hydrogen gas stream at 1500° F for 6 hr prior to compacting.

[e]Sintered in vacuum at 4200° F for 4 hr.

[f]Presintered in hydrogen atmosphere at 2600° F for 2 hr and sintered in vacuum at 4200° F for 2 hr.

[g]Curtiss-Wright tungsten powder that contained 5 volume percent hafnia.

Extrusion. - Most of the billets were extruded in a 0.250-inch-thick-wall pressed and sintered molybdenum can in a vertical 1080-ton conventional extrusion press. Temperatures from 3700° to 4200° F were utilized with reduction ratios of 8:1 or 16:1 and ram speeds ranging from 3.6 to 14.4 inches per second (see table II). A few billets with thin (0.090 in.) or heavy-walled (0.250 in.) cans of tantalum were also extruded in this hydraulic extrusion press. Two extrusions were made with unclad billets at a reduction ratio of

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20:1 in a high-energy extrusion press at 3800° F. A variety of metals and other materials such as oxides, glass, graphite, and rubber were used as container lubricants. Oxides were also used to coat the die.

Examination and Testing

Stress-rupture tests of the extruded materials were conducted in vacuum (pressure, 5×10^{-5} torr) at different stress levels at 3000° F, and a number of tests were also run at 2500°, 3400°, 3500°, and 3800° F. Photomicrographs of the extruded bars and of the ruptured stress-rupture specimens were examined. In addition, density, hardness, grain size, and fiber length-diameter ratio were determined in an attempt to correlate these parameters with the stress-rupture life of the composites. With a few composites step-load creep tests were run in order to evaluate rapidly their strength potential and to obtain suitable stresses for short-time stress-rupture tests.

Step-load creep testing. - To obtain stress-rupture data, all materials were first tested at 3000° F in vacuum with an 8000-pound-per-square-inch load. If the specimen did not fail in a short time (less than 100 hr) and the creep rate was constant, additional loads were added every 24 hours until the specimen ruptured. A constant creep rate and the same final elongation at fracture with each load were assumed, and estimates were made of the stress required for short-time (less than 100 hr) stress-rupture tests.

The tests were conducted in a conventional beam-load machine equipped with a vacuum chamber and a tantalum heater. The machine is similar to one that is used for tensile testing and is described in reference 7. Gage length of the specimen was 1 inch, and the creep data were read with a dial gage that measured loading rod motion.

Density. - Density determinations were made by mercury displacement. An average of two runs was used. The precision of the method was nominally 0.02 gram per cubic centimeter.

Hardness. - Hardness was determined with a 136° diamond-pyramid indenter using a 200-gram load. Five readings were averaged for each determination.

Grain size. - Grain size was determined by counting the number of grains intercepted by a 48.3-centimeter circle at a magnification of 640 and by using the formula $D = C/MN$, where

D   average grain diameter, cm

C   circumference of circle, cm

M   magnification

N   number of interceptions

An average of three counts was taken for each determination.

Fiber length-diameter ratios. - Measurements of fiber lengths and diameters were made on the photomicrographs (magnification, 500) by using a fine ruler under a magnifying lens. Each figure represents an average of measurements made on 50 fibers. Several measurements were made along the length of a fiber in order to obtain a representative average value for the diameter.

Processing Variables of Extrusion

Twenty-one cold-pressed and sintered billets of tungsten and tungsten plus additive were successfully extruded, and some promising results were obtained. A number of processing variables had to be investigated in order to produce intact, dense, extruded material.

At the start of this study tungsten billets were being extruded at relatively low reduction ratios of 4:1 and 6:1 and relatively low temperatures of 3200° to 3600° F. Extrusion of tungsten and tungsten composites at higher temperatures and reduction ratios posed an obstacle to the work. One of the problems was presumed to be lubrication in the temperature range 3800° to 4400° F. To provide good lubrication, the tungsten and tungsten composites were canned in thin- or thick-walled containers of softer materials such as tantalum and molybdenum. The use of soft-metal canning materials was also considered to introduce a more nearly isostatic condition in which the extrusion pressure was distributed more uniformly around the billet. While tantalum appeared effective, it was also expensive, so thick-walled 1/4-inch molybdenum cans were produced by powder metallurgy techniques. The cans also served to protect the billet from contamination. In this manner the extrusion capability for tungsten billets was extended to higher reduction ratios (16:1) and higher temperatures (approx 4200° F).

The effect of composition and processing procedure on extrusion pressure was quite marked, as shown in table II (p. 5). Some of the comparisons of extrusion pressure required for various billets must be made carefully because there were some differences also in other variables such as extrusion temperature and lubrication. Nevertheless, it can be seen that the composites containing 8 to 10 volume percent of yttria and hafnia required lower extrusion pressures than tungsten-8 volume percent zirconia. While dual-sintered tungsten required a much lower extrusion pressure than vacuum-sintered tungsten, interpretation of the results is hampered by the difference in extrusion temperature and the use of molybdenum rather than tantalum can material. The reduction in extrusion pressure required for the dual-sintered tungsten by additions of zirconia, hafnia, and thoria is clearly shown. The reduction obtained with yttria is not as marked as that shown in the case of the other three oxides. The results for billet 17, tungsten with 16 volume percent thoria, are obscured by the fact that 15 seconds were required to transfer the billet from the furnace to the extrusion die. A larger extrusion pressure was required for the Curtiss-Wright tungsten - 5-volume-percent-hafnia billet (billet 15) to which 18.5 volume percent hafnia was added (total hafnia, 23.5

volume percent) than for the tungsten - 25.5-volume-percent-hafnia composite made with General Electric tungsten, despite the fact that both billets contained about the same amount of oxide.

The extrusion pressure required for tungsten was raised by the addition of the refractory compounds. The highest pressure was required for the tungsten - hafnium carbide composite and the lowest for the tungsten - hafnium boride composite, while the requirements for tungsten - hafnium nitride and tungsten - tantalum carbide were of the same order of magnitude. The pressures required ran from 16 000 to 82 000 pounds per square inch above that needed for the unreinforced material.

RESULTS

Fibering and Length-Diameter Ratios

Photomicrographs of transverse and longitudinal sections of the extruded materials (figs. 1 to 4) showed that some degree of fibering was achieved with all of the additives. In general, the oxides were more effectively fibered than the refractory compounds. From the microstructures it was noted that the extent of the elongation varied with the degree of deformation throughout the extruded bar and was greater at the middle than at the nose of the bar and greater at the edges than at the middle. Comparisons of elongation (length-diameter ratio L/D) of the additives were made from microstructures at the middle of the bar, and these are also representative of the specimens used for stress-rupture testing.

Figures 1(c), (d), (e), and (f) show longitudinal sections of composites with 8 to 10 volume percent of zirconia, yttria, hafnia, and thoria, respectively. For purposes of comparison, figure 1(a) is a view of unreinforced tungsten, and figure 1(b) is a view of tungsten - 8 volume percent zirconia, which is typical of the transverse-section views obtained with all the oxides. Inspection of the photomicrographs of the oxide composites shows that substantial fibering was obtained with the zirconia, yttria, and hafnia; however, the thoria was not elongated as effectively as the other oxides. When the L/D measurements (table III, p. 16), which are more quantitative than visual observation, are used, it is evident that, with the 8- to 10-volume-percent oxides, the hafnia ($L/D = 23.3$) was more elongated, and the yttria ($L/D = 12.7$) less elongated, than the zirconia ($L/D = 19.1$); thus, the overall order of elongation from highest to lowest is hafnia, zirconia, yttria, and thoria.

Figures 1(g) to (l) show transverse and longitudinal sections of tungsten extrusions with higher oxide concentrations, 14.5 to 25.5 volume percent. These composites as noted in table II have also been extruded at 4200° F and a reduction ratio of 8:1. The elongation of the oxides is readily observed in all of the longitudinal sections. While it is difficult to make comparisons on inspection, it does appear that, when the oxide concentration was increased from 8.0 to about 15.0 volume percent in the zirconia and thoria composites, the extent of elongation increased. With additional oxide, 20.5 to 25.5 volume percent of zirconia, yttria, and hafnia, marked agglomeration was noted, and
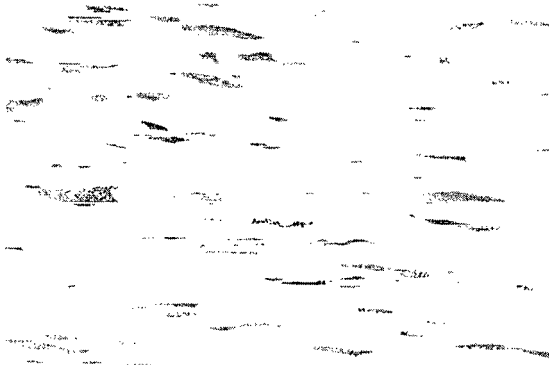
8

Cross sections

(a) Unreinforced tungsten.
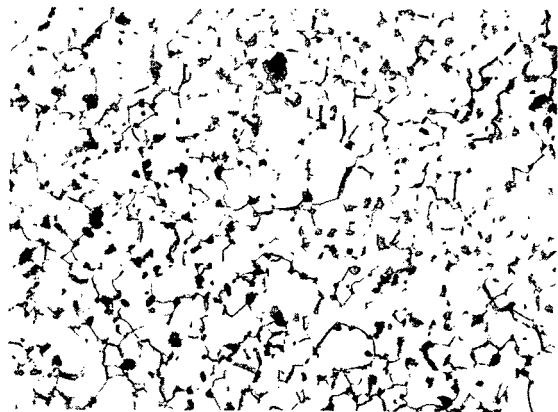
(b) Tungsten – 8 volume percent zirconia.

Longitudinal sections

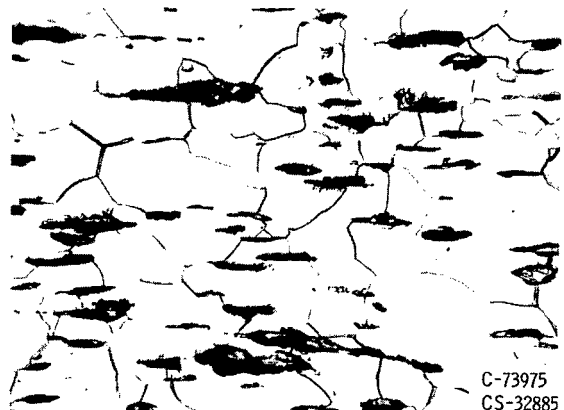(c) Tungsten – 8 volume percent zirconia.

(d) Tungsten – 8 volume percent yttria.

Longitudinal sections
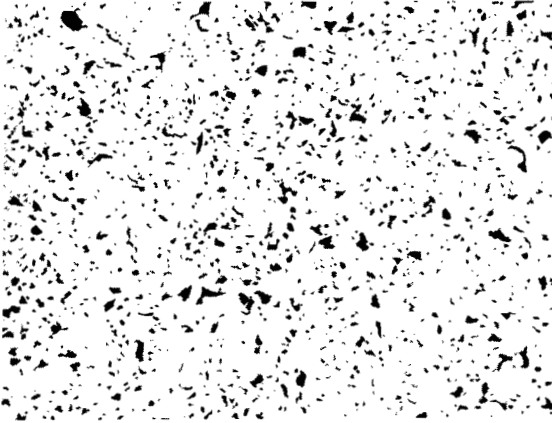
(e) Tungsten – 10 volume percent hafnia.
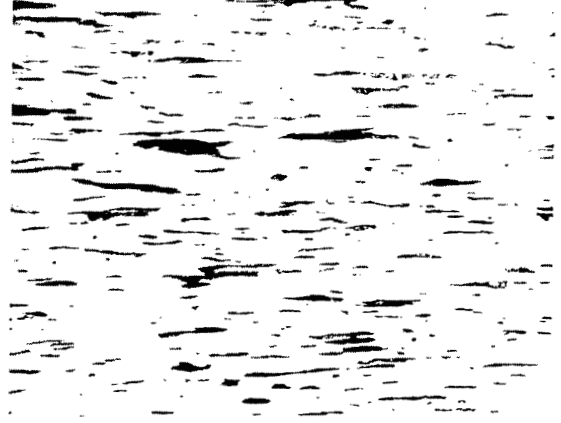
(f) Tungsten – 8 volume percent thoria.

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Figure 1. – Microstructures of as-extruded tungsten and tungsten-oxide composites. X500. (Reduced 30 percent in printing.)
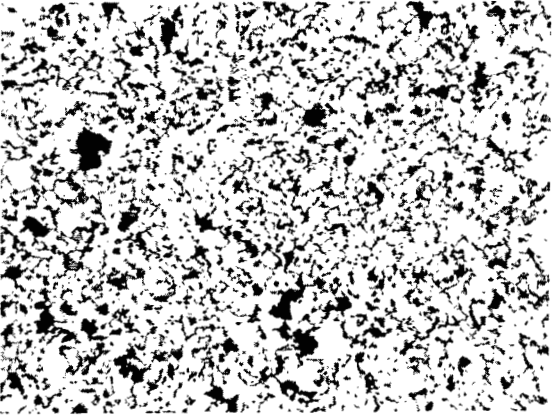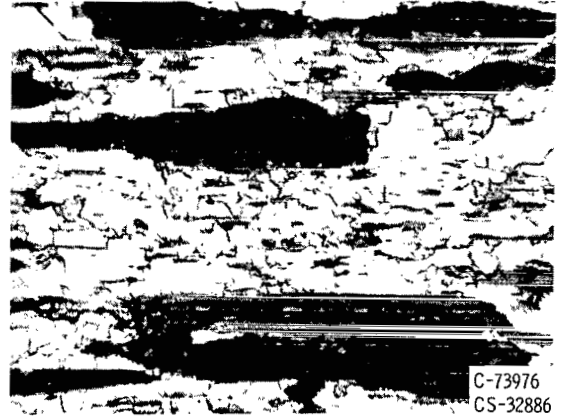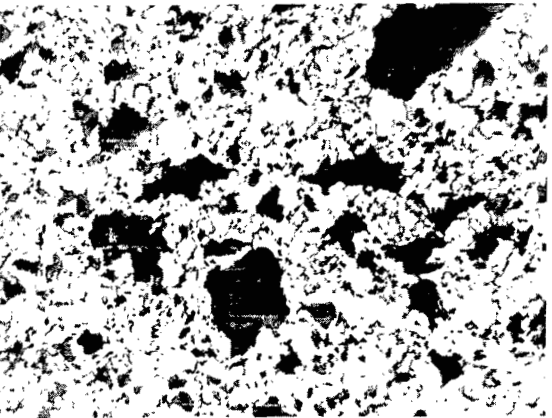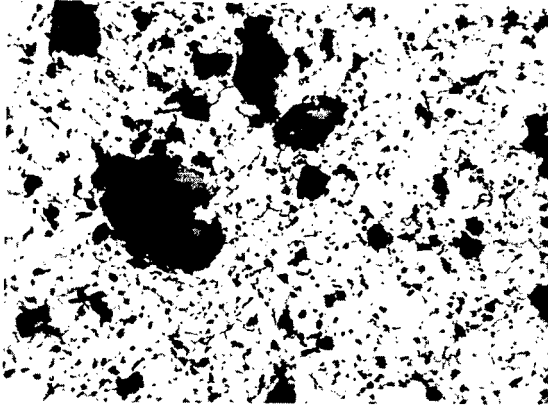
9

(g) Tungsten - 14.5 volume percent zirconia.

(h) Tungsten - 20.5 volume percent zirconia.
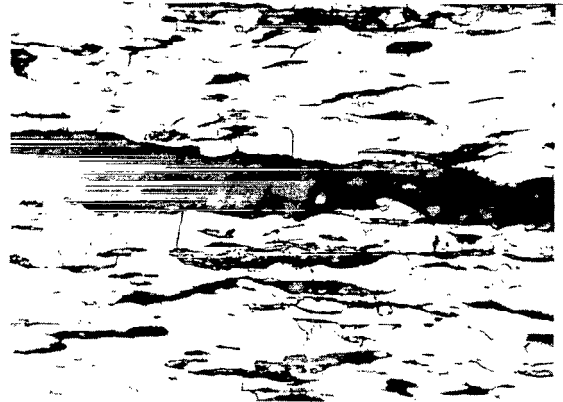

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(i) Tungsten - 20.5 volume percent yttria.

Figure 1. - Continued. Microstructures of as-extruded tungsten and tungsten-oxide composites. X500. (Reduced 30 percent in printing.)

(j) Tungsten - 25.5 volume percent hafnia.

(k) Tungsten - 23.5 volume percent hafnia.

(l) Tungsten - 16 volume percent thoria.

Figure 1. - Concluded. Microstructures of as-extruded tungsten and tungsten-oxide composites. X500. (Reduced 30 percent in printing.)
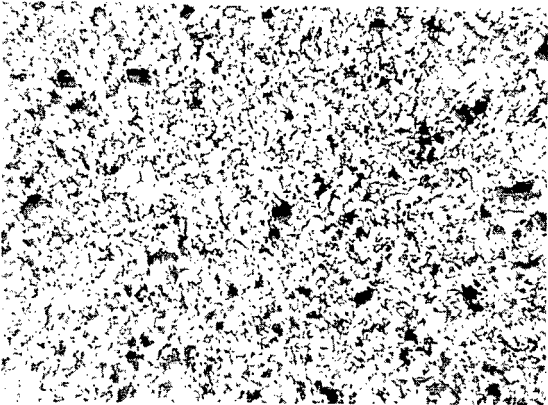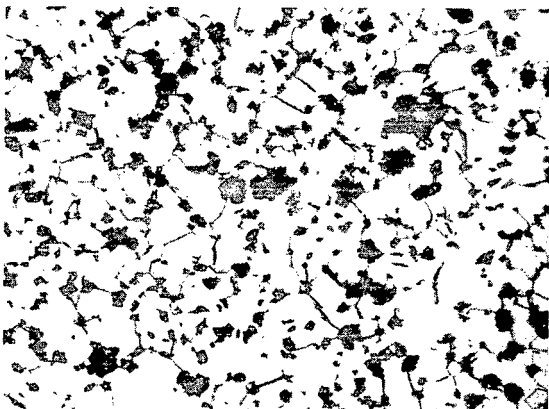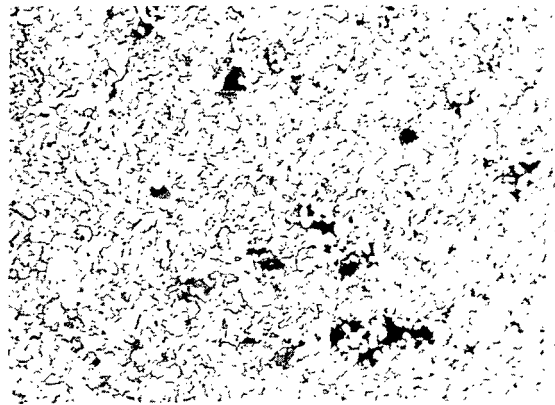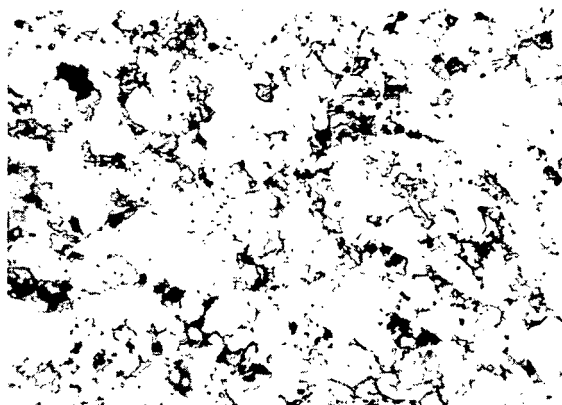
Cross sections

Longitudinal sections from nose of extruded bar
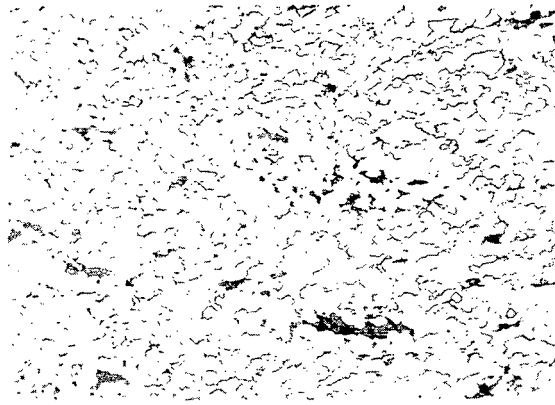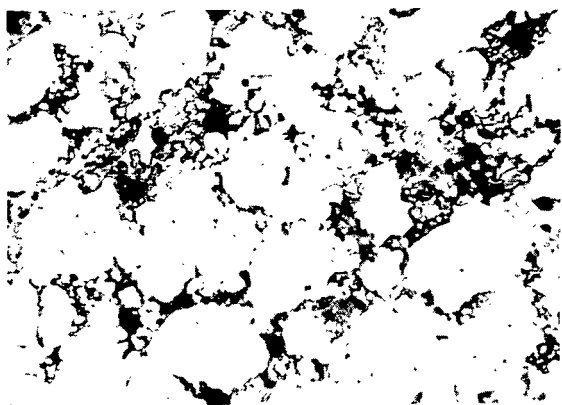
Longitudinal sections from middle of extruded bar

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(a) Tungsten - 8 volume percent hafnium boride.　　　　　(b) Tungsten - 8 volume percent hafnium nitride.

Figure 2. - Microstructures of as-extruded tungsten - refractory-compound composites.　X500.　(Reduced 30 percent in printing.)

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Cross sections

Longitudinal sections from nose of extruded bar

Longitudinal sections from middle of extruded bar

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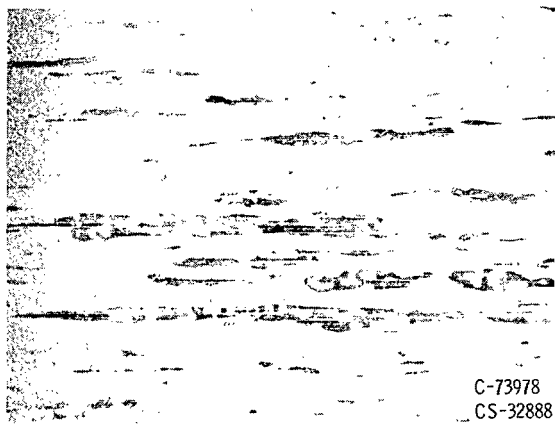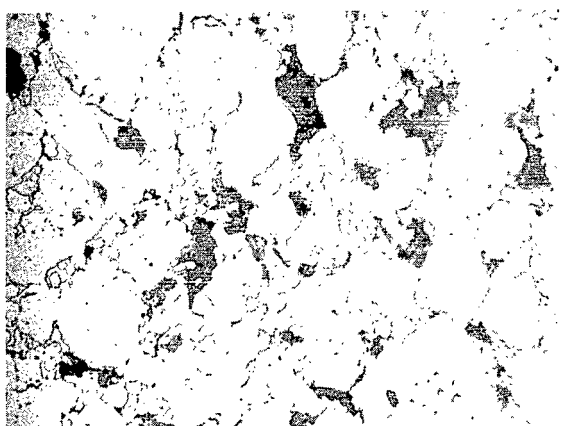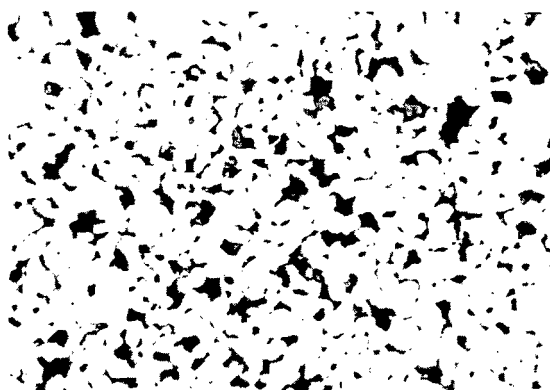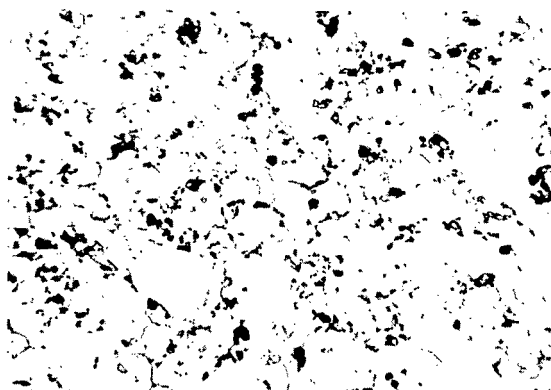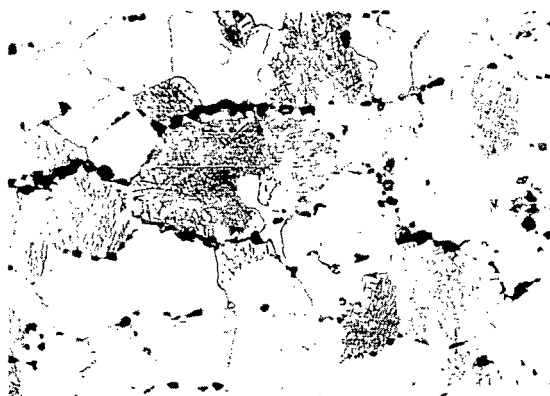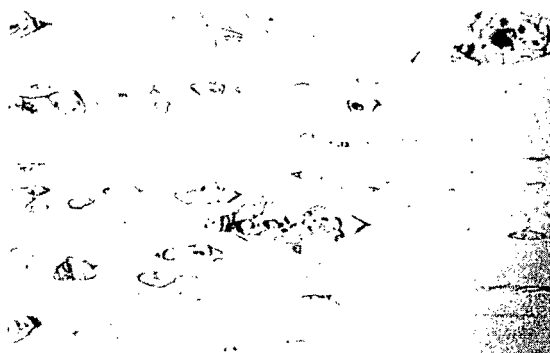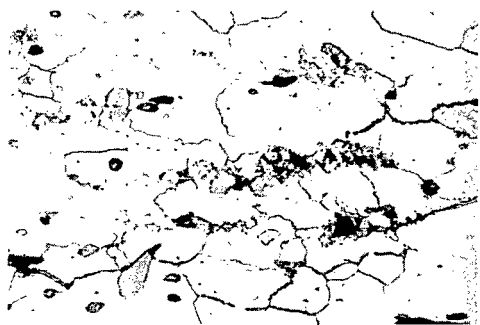(c) Tungsten - 8 volume percent hafnium carbide.   (d) Tungsten - 8 volume percent tantalum carbide.

Figure 2. - Concluded. Microstructures of as-extruded tungsten - refractory-compound composites. X500. (Reduced 30 percent in printing.)

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Figure 3. - Microstructure of tungsten - hafnium boride composite. Longitudinal section from center to edge of bar. X500. (Reduced 30 percent in printing.)

the extent of fibering decreased. It is also apparent from figures 1(j) and (k) that billet 15, with 23.5 volume percent hafnia, made with a matrix of Curtiss-Wright tungsten - 5 volume percent hafnia retained a smaller grain size and had less agglomeration than billet 14, with 25.5 volume percent hafnia, made under the same processing conditions with the unreinforced tungsten powder.

Finally, figure 2 shows transverse and longitudinal sections of tungsten - refractory-compound composites, billets 18 to 21, also extruded at 4200° F with a reduction ratio of 8:1. Two photomicrographs of longitudinal sections are given from each bar, one at the nose and one farther back in the bar since the nose is less deformed. It can be readily seen from the photomicrographs that the hafnium nitride is the most effectively fibered in this group and is more highly elongated toward the middle than at the nose of the bar. While the hafnium carbide appeared elongated in the longitudinal sections of the composite, it had cracks in it that may have been partly responsible for the elongated appearance.

The tantalum carbide composite shows an unusual microstructure at the nose of the bar (fig. 2(d)), which is not typical of the rest of the extrusion, and this is considered in the DISCUSSION. The tantalum carbide is noticeably deformed in the middle section, although the elongation is small compared with that of hafnium nitride. The one case in which no elongation is evident in either the nose or the middle of the bar is that of the hafnium boride composite. Fibering can be seen, however, at the more highly deformed edges of the extruded bar (fig. 3). Thus, with the refractory-compound composites, in most cases there was a small elongation at the nose of the extrusion bars, the fibering increased toward the middle of the bars, and the order of elongation from highest to lowest was hafnium nitride, hafnium carbide (cracked), tantalum carbide, and hafnium boride. It is interesting to note that, with 8 volume percent of additive, the elongation of the hafnium nitride (L/D = 18.4) was almost as great as that obtained with zirconia (L/D = 19.1), despite the wide difference in their melting points.

A series of photomicrographs shown in figure 4 illustrates the effect of reduction ratio of fiber elongation. Figures 4(a) and (b) show the microstructures of sections taken from the nose and the middle of the tungsten - 8-volume-percent-zirconia bar. Figure 4(a) shows the relatively unreduced front section (reduction ratio, < 8:1), and figure 4(b) shows the fully reduced middle section. Figures 4(c) and (d) are photomicrographs of tungsten - 5 volume percent zirconia with reduction ratios of 16:1 and 20:1. The obvious differences in elongation can be seen on inspection. The measured L/D values are 6.9 for the nose of the bar with a reduction ratio of 8:1 and 19.1, 24.5, and 29.3 for the middle of the bars with reduction ratios of 8:1, 16:1, and 20:1, respectively.

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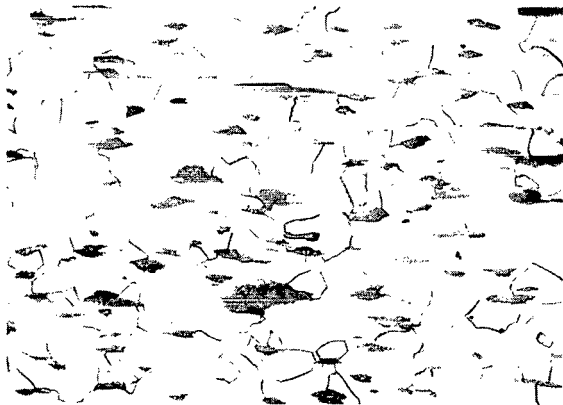
(a) Nose of bar of tungsten - 8 volume percent zirconia. Reduction ratio, 8:1; length-diameter ratio, 6.9.
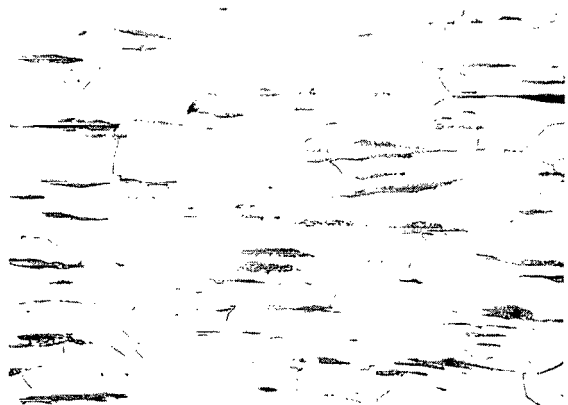
(b) Middle of bar of tungsten - 8 volume percent zirconia. Reduction ratio, 8:1; length-diameter ratio, 19.1.
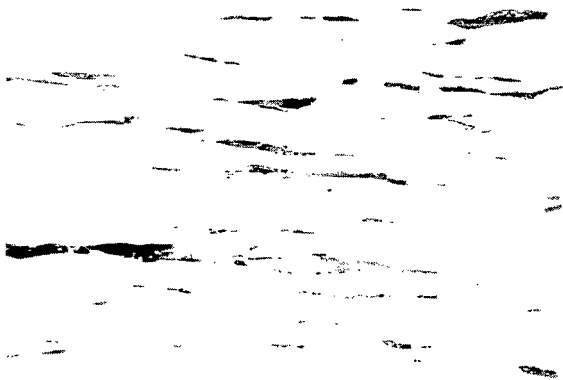
(c) Middle of bar of tungsten - 5 volume percent zirconia. Reduction ratio, 16:1; length-diameter ratio, 24.5.

(d) Middle of bar of tungsten - 5 volume percent zirconia. Reduction ratio, 20:1; length-diameter ratio, 29.1.

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Figure 4. - Microstructures of as-extruded tungsten-zirconia composites. Longitudinal sections. X500. (Reduced 30 percent in printing.)

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TABLE III. - EXPERIMENTAL RESULTS

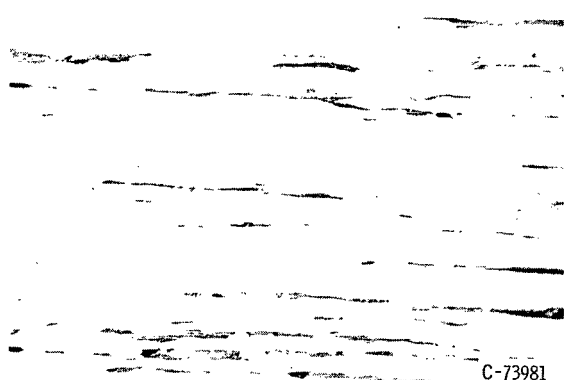| Billet	Composition	Temperature, °F	Stress, psi	Stress-rupture life, hr	Fiber length-diameter ratio	Theoretical density, percent	Diamond pyramid hardness Transverse	Longitudinal	Average grain diameter of matrix, cm Transverse	Longitudinal
1	Tungsten	3000	8 000	1.9	----	99.32	376	360	0.0040	0.0040
2	Tungsten	3000	8 000	1.5	----	99.51	383	371	0.0028	0.0045
			8 000	2.6						
			5 000	53.8						
			3 000	348.7						
3	Tungsten - 8 volume percent zirconia	3000	8 000	8.0	19.1	99.37	371	396	0.0016	0.0023
		3000	8 000	12.1						
		3000	5 000	74.5						
		3800	3 000	4.3						
4	Tungsten - 8 volume percent yttria	3000	8 000	7.2	12.7	99.86	401	377	0.0019	0.0025
			8 000	9.7						
			7 000	23.5						
			6 000	44.9						
			4 000	161.0						
		3400	3 000	25.5						
		3800	3 000	1.6						
5	Tungsten - 10 volume percent hafnia	3000	8 000	10.1	23.3	100.16	410	420	0.0022	0.0030
		3000	8 000	10.6						
		3000	5 000	261.4						
		3400	3 000	34.7						
6	Tungsten - 5 volume percent zirconia	3000	8 000	4.4	12.5	99.04	---	399	------	0.0020
		3000	8 000	3.1						
7	Tungsten - 5 volume percent zirconia	3000	8 000	3.6	29.3	93.71	---	384	------	0.0018
		3000	8 000	4.3						
		3000	8 000	5.4						
8	Tungsten	3000	8 000	21.6	----	99.60	369	369	0.0047	0.0045
	Tungsten (swaged 50 percent)	3000	8 000	11.8	----	-----	429	446	0.0017	0.0042
		3000	8 000	14.7						
9	Tungsten	3000	8 000	20.1	----	99.68	383	380	0.0023	0.0026
		3000	8 000	29.1						
10	Tungsten	3000	8 000	18.9	----	-----	---	---	------	------
11	Tungsten - 14.5 volume percent zirconia	3000	8 000	1.9	23.8	99.69	441	423	0.0009	0.0014
				1.7						
				1.0						
				1.6						
12	Tungsten - 20.5 volume percent zirconia	3000	8 000	2.0	10.4	a101.10	459	440	0.0008	0.0011
		3000	8 000	1.6						
13	Tungsten - 20.5 volume percent yttria	3000	8 000	1.7	6.8	a100.~2	413	419	0.0009	0.0011
		3000	8 000	1.3						
		3000	8 000	2.4						
14	Tungsten - 25.5 volume percent hafnia	3000	8 000	8.8	14.1	a97.20	466	458	0.0010	0.0020
		3000	8 000	6.2						
15	Tungsten - 23.5 volume percent hafnia[b]	3000	8 000	4.9	16.7	a101.10	578	515	0.0005	0.0007
				4.7						
				4.3						
				5.4						
16	Tungsten - 8 volume percent thoria	3000	8 000	34.2	7.8	99.22	381	389	0.0026	0.0036
17	Tungsten - 16 volume percent thoria	3000	8 000	36.9	13.2	98.66	420	418	0.0012	0.0013
18	Tungsten - 8 volume percent hafnium boride	3000	8000 to 20 000	c223.3	1.0	a95.63	385	425	0.0011	0.0024
		3000	8 000	d545.0						
		3000	18 000	83.5						
		3000	28 000	3.2						
		3500	8 000	4.0						
		2500	28 000	323.9						
19	Tungsten - 8 volume percent hafnium nitride	3000	8000 to 10 000	c292.2	18.4	98.50	543	471	0.0006	0.0007
		3000	8 000	d388.0						
		3000	12 000	101.1						
		3000	18 000	21.5						
		3500	8 000	4.2						
		2500	24 000	e>45.4						
20	Tungsten - 8 volume percent hafnium carbide	3000	8000 to 18 000	c164.9	6.6	95.13	41?	406	0.0013	0.0014
		3000	8 000	d1145.0						
		3000	18 000	77.9						
21	Tungsten - 8 volume percent tantalum carbide (nose of bar)	3000	8000 to 14 000	c414.6	----	-----	412	406	0.0012	0.0013
		3000	8 000	d920.0						
	Tungsten - 8 volume percent tantalum carbide (middle of bar)	3000	8 000	788.6	5.1	99.44	31?	372	0.0011	0.0033
		2500	12 000	487.9						

a Questionable because of changes in theoretical density.
b 14.5 Volume percent hafnia was added to Curtiss-Wright tungsten powder already containing 5 volume percent hafnia.
c Total time with increasing load (see table IV).
d Estimated time from creep data in table IV.
e Test incomplete - specimen support rod on stress-rupture machine failed.

Evidence of multiphased and unusual microstructure can be seen in the color, texture, and shape of some of the additives. In the case of the hafnium boride composite, the additive has light and dark areas, and a yellow phase appears in the grain boundaries. In the hafnium nitride composite, the additive shows a white area surrounding a gray area with small black areas in the gray. In the hafnium carbide composite, in addition to the slightly elongated light-gray cracked material, there is evidence of a small amount of a highly elongated, intact, dark-gray phase. In the tantalum carbide composite, the microstructure suggests the presence of a matrix surrounded by carbide loops.

Stress-Rupture Results

The results of stress-rupture testing of the as-extruded tungsten and the tungsten composites are given in table III and figures 5 to 12. For convenience the stress-rupture data will be presented for several compositions, unreinforced tungsten, tungsten with low oxide (5 to 10 volume percent), tungsten with high oxide (14.5 to 25.5 volume percent), and tungsten with refractory compounds (8 volume percent), and for variations in stress-rupture properties with load, temperature, and processing conditions.

Unreinforced tungsten. - Specimens from five extruded tungsten billets (billets 1, 2, 8, 9, and 10) made with small differences in the method of processing (see table II, p. 5) were stress-rupture tested, and the results are shown in figure 5 and table III. The stress-rupture life of unreinforced tungsten at 3000° F and 8000 pounds per square inch in vacuum varied from 1.5 to 29.1 hours. The most significant variable was the sintering schedule. Billets sintered in a vacuum at 3500° and 4200° F (billets 1 and 2) had stress-rupture lives of 1.5 to 2.6 hours, respectively. Those sintered at 2600° F in hydrogen followed by vacuum sintering at 4200° F (billets 8, 9, and 10) gave stress-rupture lives at the same load and temperature of 18.9 to 29.1 hours.

The specimens made with hydrogen-precleaned powder showed no significant difference in stress-rupture life from those in which the powder was not cleaned. Also, billets 9 and 10, extruded at a reduction ratio of 16:1 in a molybdenum or tantalum can, respectively, showed very little difference in stress-rupture life from billet 8, extruded at a reduction ratio of 8:1 in a molybdenum can.

Tungsten plus low volume percent oxides. - Stress-rupture results of the low oxide composites (8 to 10 volume percent) are also given in table III and figure 5. Most of the observations of the effect of low-volume-percent oxide additions to tungsten are drawn from billets 3, 4, 5, and 16, which contained 8 to 10 volume percent of zirconia, yttria, hafnia, and thoria, respectively. The stress-rupture lives of these composites at 3000° F and 8000 pounds per square inch in vacuum ranged from 7.2 to 34.2 hours. It is evident from table III that the specimens with 8 to 10 volume percent oxide (billets 3, 4, and 5) show a fourfold to fivefold increase in stress-rupture life when compared with unreinforced tungsten (billet 1) prepared under the same conditions by vacuum sintering. The tungsten - 8-volume-percent-thoria composite prepared with a hydrogen presinter (billet 16) had three to four times the stress-
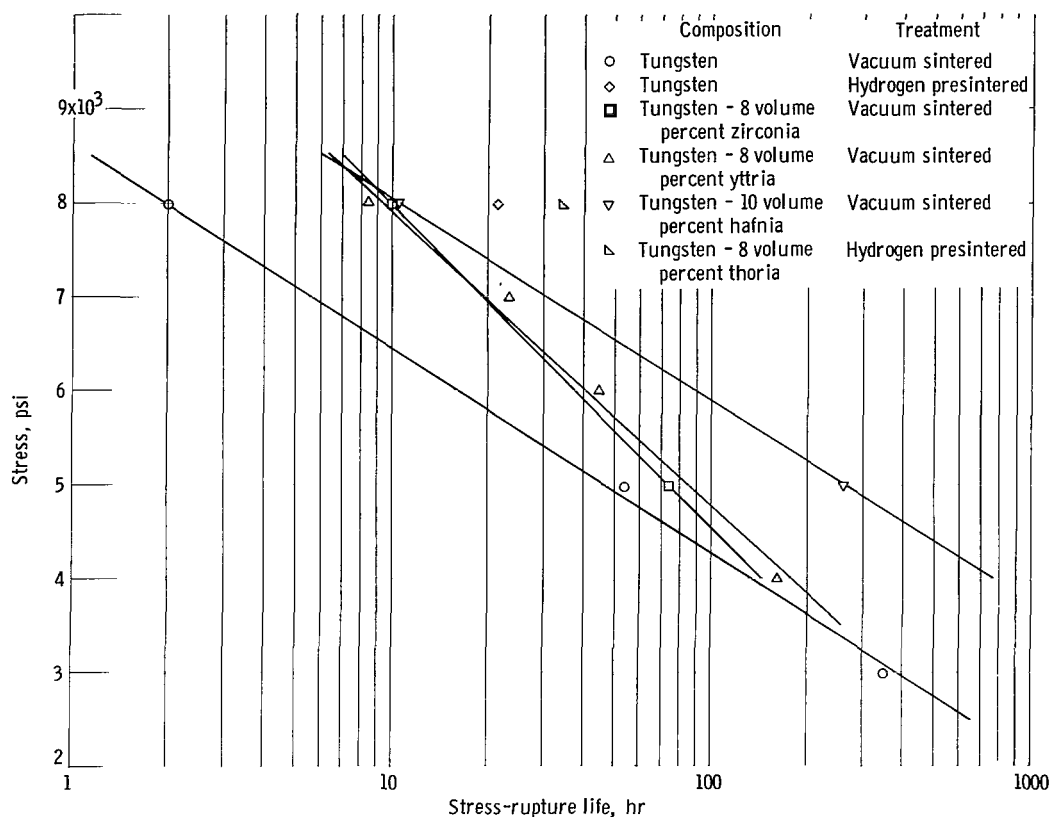
Figure 5. - Stress-rupture strength of tungsten and tungsten-oxide composites at temperature of 3000° F.

rupture life of the other oxide composites; however, it was only slightly stronger, with less than a twofold advantage, than the unreinforced tungsten (billet 8) that was prepared in the same way with a hydrogen presinter.

Because of the difficulties in machining, many stress-rupture specimens were damaged, and the data were therefore limited in most cases to one or two values. With the composites containing 8 volume percent zirconia, 8 volume percent yttria, and 10 volume percent hafnia, however, a few specimens were available for tests made at several stresses and temperatures. Figure 5 shows that, under high-stress, short-life conditions, the vacuum-sintered tungsten-zirconia and tungsten-yttria composites were considerably better than the vacuum-sintered unreinforced tungsten. The tungsten-hafnia composite maintained its strength advantage and was better than unalloyed tungsten throughout the stress range. Figure 6 shows stress-rupture results plotted against temperature. Above 3500° F the tungsten-zirconia and tungsten-yttria composites were better in stress-rupture life than the tungsten-hafnia composite; however, extrapolated values of stress-rupture life at 3000° F show the tungsten-hafnia composite to have a distinct advantage in strength at this temperature.

Tungsten plus high volume percent. - The stress-rupture results for the tungsten composites of 14.5 to 25.5 volume percent oxide are given in table III (p. 16) and figure 7. The stress-rupture life at 8000 pounds per
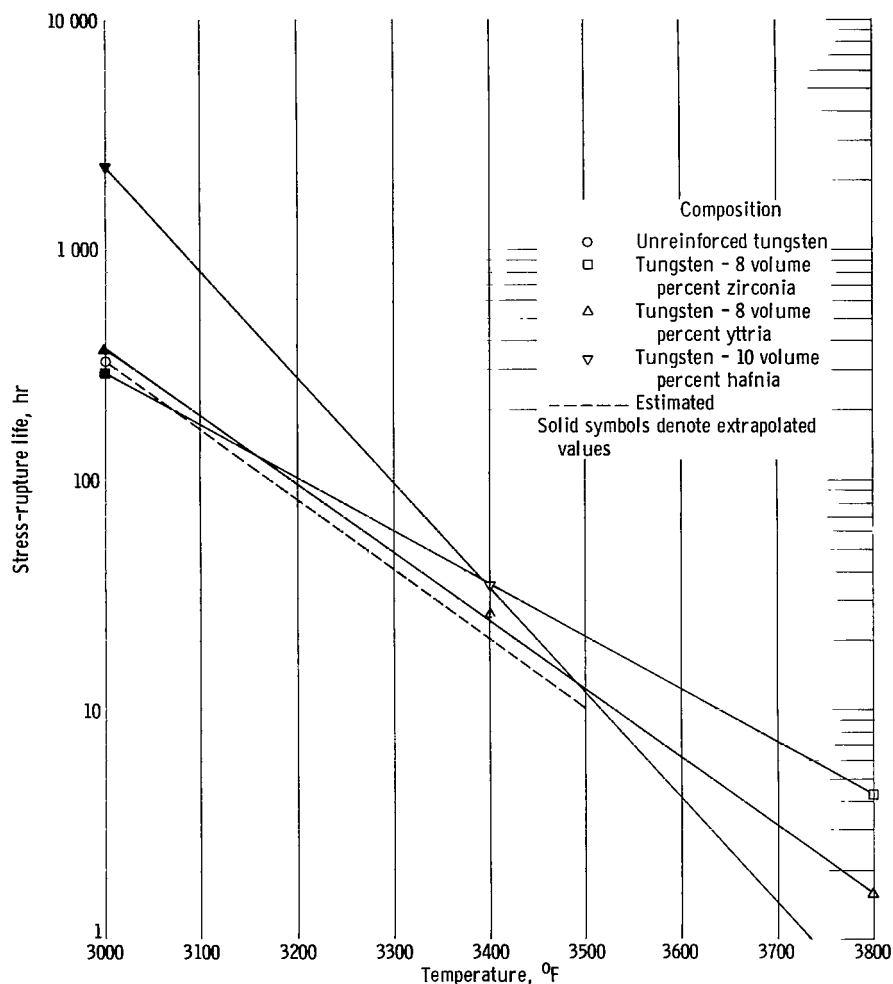
18

Figure 6. - Effect of temperature on stress-rupture life of tungsten-oxide composites at stress of 3000 pounds per square inch.

square inch and 3000° F varied from 1 to 36.9 hours. In this group the best results were obtained with the tungsten-thoria composite. In all other cases with high volume percent oxides the stress-rupture lives of the composites were less than that of the tungsten despite the fact that all the billets had received the hydrogen presinter. It can also be seen that the composites containing hafnium oxide in a matrix of tungsten or tungsten - 5 volume percent hafnia were again somewhat stronger in stress-rupture than the tungsten-zirconia and tungsten-yttria composites at 3000° F. It should be noted that the greatest difficulty in machining and the poorest recovery of intact extruded material occurred in this group of extrusions. Thus, with different machining practice it is possible that the high-volume-percent-oxide specimens may prove to have greater inherent strength.

Tungsten plus 8 volume percent refractory compounds. - The stress-rupture results for the tungsten - refractory-compound composites showed uniformly good results (table III, p. 16, and figs. 7 to 12). The stress-rupture lives
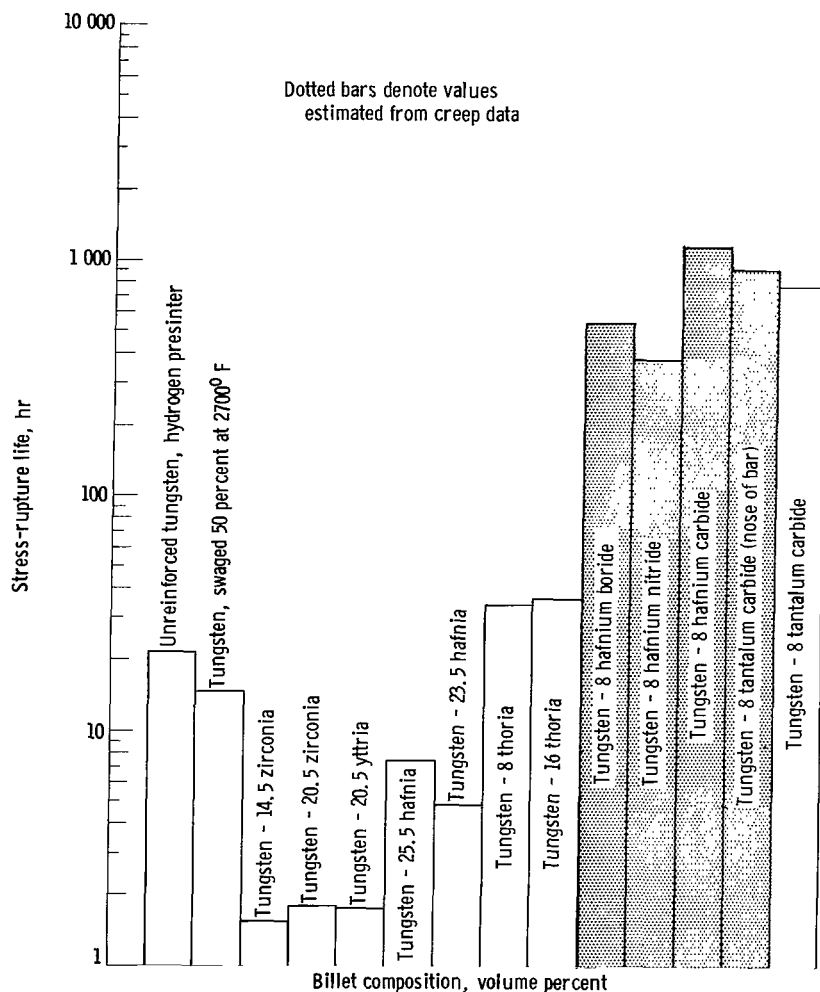
Figure 7. - Stress-rupture life of tungsten, tungsten-oxide, and tungsten - refractory-compound composites. Temperature, 3000° F; stress, 8000 pounds per square inch.

at 3000° F and 8000 pounds per square inch of the tungsten - hafnium boride, nitride, or carbide composites and the tantalum carbide composites were at least an order of magnitude greater than those for the unreinforced material. Because of the length of time required for testing, some of the stress-rupture results have been estimated from creep data. While the composites containing hafnium boride and hafnium carbide had greater stress-rupture lives than the composites containing the hafnium nitride and tantalum carbide, the latter two composites had better ductility, as revealed by the elongation and reduction in area.

Creep Properties

When the stress-rupture data were obtained, all materials were first tested at 3000° F in vacuum with an 8000-pound-per-square-inch load. Because of the exceptional properties of some of the tungsten composites, the time
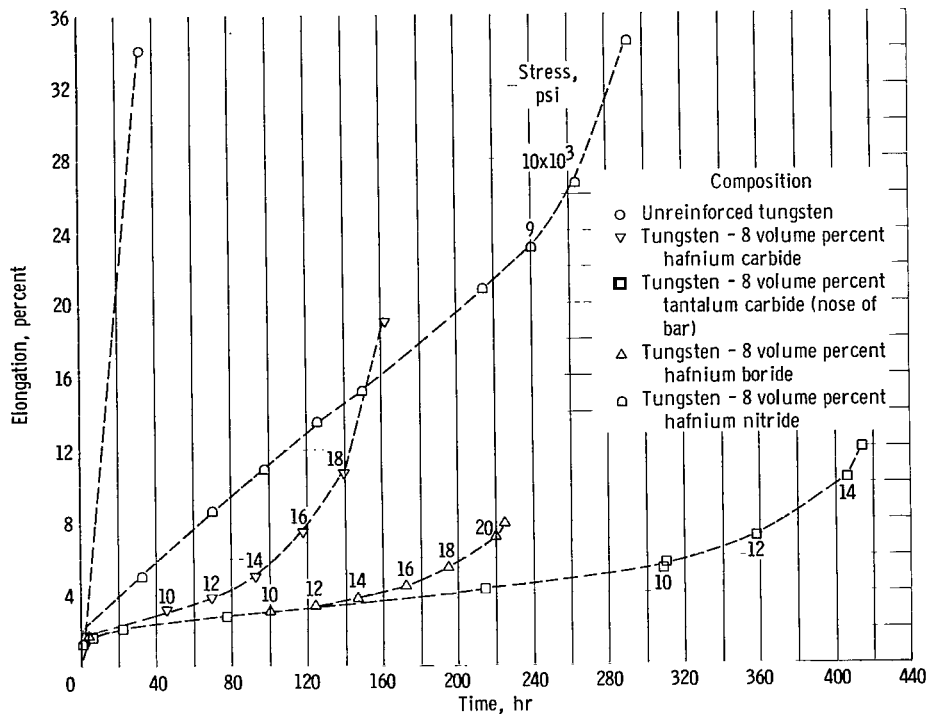
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Figure 8. - Step-load creep curves for tungsten - refractory-compound composites at temperature of 3000° F.

required to fracture the stress-rupture specimens with an 8000-pound-per-square-inch load proved to be unusually long, so the load was increased to accelerate the test. The first specimen tested in this manner was a tungsten - 8-volume-percent tantalum carbide specimen taken from the nose of the extrusion bar, which had a creep rate two orders of magnitude lower than materials previously tested at 3000° F and 8000 pounds per square inch and a life of over 300 hours. Because of the limited amount of equipment for long-term testings, it was felt that the test should be accelerated, and, therefore, increased loads were applied during the test. The curves of figure 8 are plots of the points at which the loads were increased and the slope of the elongation as a function of time for each material that was tested in this manner.

Other composites, namely, tungsten - 8 volume percent hafnium boride, hafnium carbide, and hafnium nitride, also had unusually low creep rates, as evidenced by earlier portions of the creep-rupture tests. Table IV shows creep rates obtained at different loads. The creep rate at 3000° F with an 8000-pound-per-square-inch load was 2.88×10^{-8} per second for tungsten - hafnium boride, 4.28×10^{-8} per second for tungsten - hafnium carbide, and 2.55×10^{-7} per second for tungsten - hafnium nitride. The order for total elongation before fracture was tungsten - hafnium nitride, tungsten - hafnium carbide, and tungsten - hafnium boride, the nominal percentages being 35, 18, and 8, respectively. The elongation and creep rate for tungsten - tantalum carbide from the middle of the bar were of the same order as for tungsten - hafnium nitride. Raising the load from 8000 to 10 000 pounds per square inch at 3000° F increased

TABLE IV. - STEP-LOAD CREEP DATA AT 3000° F

Billet	Composition	Second-stage creep elongation, mils	Load, psi	Time, hr	Creep rate		Increase in creep rate, percent	Stress-rupture life estimated from fig. 8, hr	Calculated stress-rupture life, hr
					mils/hr	sec^{-1}			
18	Tungsten - 8 volume percent hafnium boride	54	8 000	100.0	0.104	2.88×10^{-8}	-----	545.0	538.0
			10 000	124.0	.141	3.91	35.6	375.0	383.0
			12 000	148.0	.150	4.15	6.3	330.0	359.0
			14 000	172.0	.253	7.01	69.6	207.0	213.5
			16 000	196.0	.450	1.25×10^{-7}	77.9	135.0	120.0
			18 000	220.0	.725	2.01	61.2	77.0	74.6
			20 000	[a]223.3					
19	Tungsten - 8 volume percent hafnium nitride	310	6 000	239.1	0.921	2.55×10^{-7}	-----	388.0	337.0
			9 000	264.1	1.41	3.91	53.1	205.0	220.0
			10 000	[a]292.2	1.95	5.40	38.3	109.0	159.0
20	Tungsten - 8 volume percent hafnium carbide	170	8 000	44.0	0.153	4.28×10^{-8}	-----	1145.0	1110.0
			10 000	68.0	.250	7.00	63.3	638.0	679.0
			12 000	92.0	.510	1.42×10^{-7}	104.0	330.0	333.0
			14 000	116.4	.884	2.47	73.3	182.0	192.0
			16 000	140.4	1.41	3.91	59.5	124.0	120.0
			18 000	[a]164.9	----	----	-----	-----	-----
21	Tungsten - 8 volume percent tantalum carbide (nose of bar)	100	8 000	310.5	0.111	3.08×10^{-8}	-----	920.0	900.0
			10 000	359.5	.265	7.36	138.8	370.0	378.0
			12 000	407.8	.655	1.82×10^{-7}	147.0	150.0	152.0
			14 000	[a]114.6	2.05	5.70	221.5	-----	-----

[a]Failed.

the creep rate of tungsten - hafnium boride 35.6 percent and of tungsten - hafnium carbide 63.3 percent, while a similar increase in load for unreinforced tungsten and tungsten alloys increased the creep rate from two to five times. Also, it is interesting to note that the creep rate for the tungsten - hafnium boride composite with an 18 000-pound-per-square-inch load was less than that for unreinforced tungsten and many tungsten alloys with an 8000-pound-per-square-inch load at the same temperature.

In order to select stresses that would permit the construction of stress-rupture curves for the high-strength composites with a minimum number of test specimens, the creep rates indicated in table IV for the different stress levels were used. By making the assumptions that the same final elongations of the stress-rupture specimens would be obtained with the different loads, and that the rate of elongation would remain constant with any one load during second-stage creep, estimates of the stress-rupture life with a fixed load could be made both graphically and mathematically. The predicted stress-rupture lives determined in this way are also presented in table IV.

Caution should be used in interpreting the creep data. Not only is it not always possible to correlate stress-rupture life with creep rates, but the method used for this study was to some degree qualitative; that is, the creep data were read with a dial gage that measured loading rod motion. Furthermore, total elongation at a high stress level may be considerably greater than at low levels. Nevertheless, the calculated stress-rupture lives obtained from the
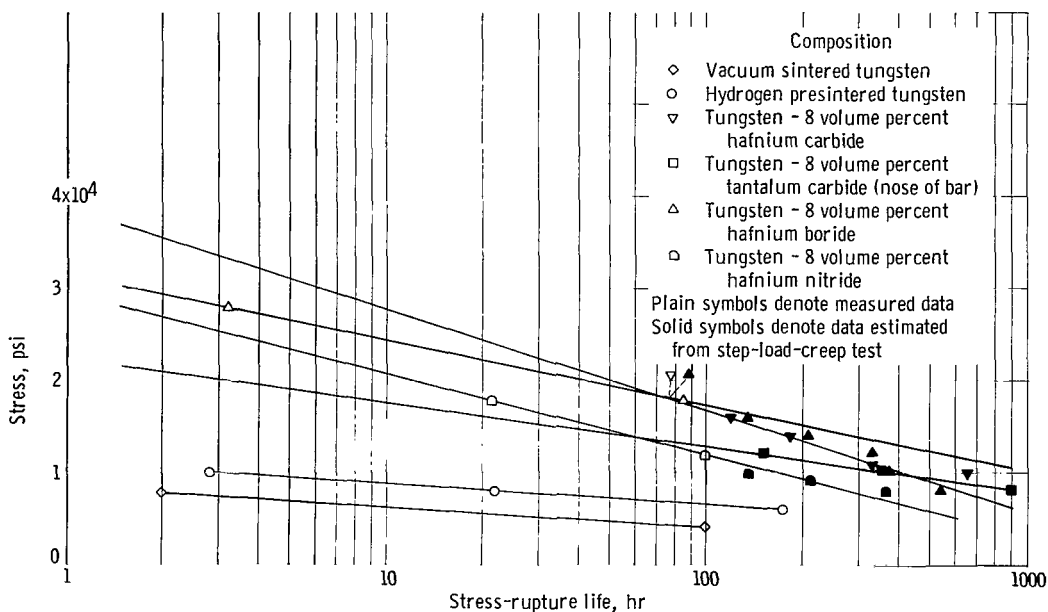
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Figure 9. - Stress-rupture life of tungsten - refractory-compound composites at temperature of 3000° F.

creep rates were useful approximations that indicated that the materials were unusually strong at elevated temperatures and helped to predict stress levels at which conventional single-load stress-rupture tests should be run on other specimens. Fortunately, it was found that stress-rupture tests with single loads of the three tungsten - hafnium-compound composites ran very close to the times estimated from step-load creep data (fig. 8) and fell almost exactly on the predicted curves (fig. 9). The stress for the 100-hour rupture life obtained from the curves in figure 9 is shown in figure 10. These permit ready comparison of the strengths of the composites obtained in the study with one of the best alloys obtained by other investigators (ref. 8). Figure 11 gives data of stress-rupture tests made at 2500° to 3500° F. The data plotted in figure 12 illustrate the temperature stability of two of the tungsten - refractory-compound composites.

It was found in the course of the investigation that the specimen of tungsten - 8 volume percent tantalum carbide that was obtained from the nose of the extrusion bar was very strong in stress-rupture based on creep data. This specimen was superior in properties to the rest of the bar and was as strong in creep as some of the tungsten - hafnium-compound composites. Examination of the microstructure also showed that it was not typical of the rest of the extrusion bar. Since there was only enough material with the unusual microstructure for the step-load creep test, in this case it was absolutely essential that the extrapolation methods described previously be utilized. In view of the excellent corroboration of the method obtained with the tungsten - refractory-compound composites (hafnium boride, hafnium carbide, and hafnium nitride), it is reasonable to assume that the extrapolated curve is representative of the actual stress-rupture properties.

18x10³

Stress, psi

16

14

12

10

8

6

4

2

0

▨ Fibered composites
▦ Reacted composites

Tungsten

Tungsten - 8 zirconia

Tungsten - 8 yttria

Tungsten - 10 hafnia

Tungsten - 8 thoria

Tungsten - 8 hafnium nitride

Tungsten - 8 tantalum carbide (nose of bar)

Tungsten - 8 hafnium boride

Tungsten - 8 hafnium carbide

Tungsten - 0.5 columbium (alloy, ref. 8)
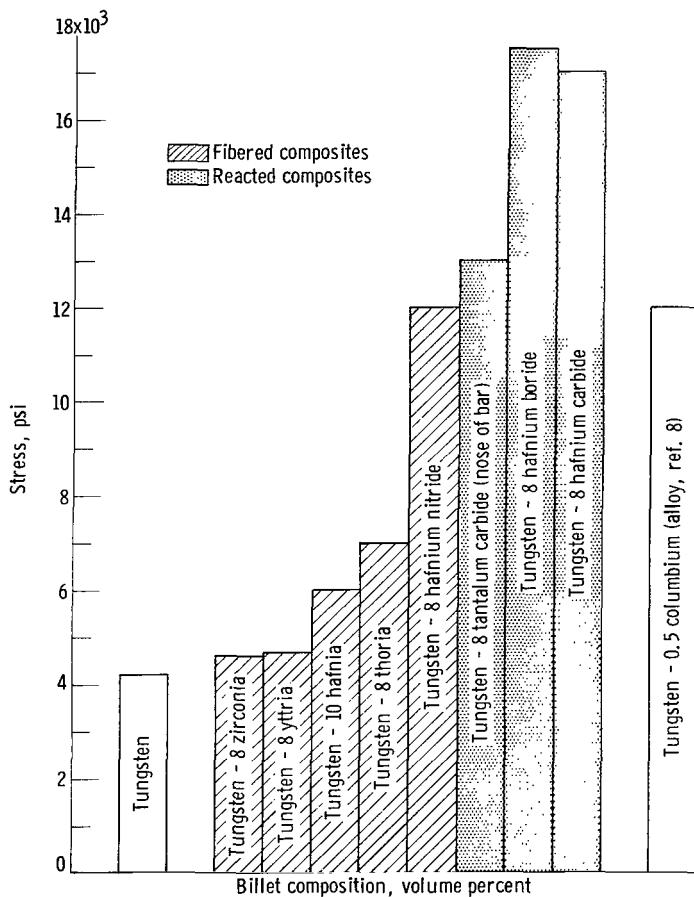
Billet composition, volume percent

Figure 10. - Stress for 100-hour stress-rupture life at temperature of 3000° F for tungsten composites.

Density

All of the density figures (table III, p. 16) with the exception of that for the tungsten - hafnium boride composite were better than 97 percent of theoretical. A number of the results are close to theoretical density. The densities of the unreinforced tungsten billets were greater than 99.32 percent of theoretical density.

With the addition of relatively low percentages of oxides, an improvement in density was obtained with yttria and hafnia, while with zirconia and thoria, the results remained the same as for the unreinforced tungsten.

High-volume-percent-oxide composites (containing over 20 volume percent oxide) had higher or lower densities than tungsten and low-volume-percent-oxide composites, the results ranging from 97 to 101 percent of theoretical density.

Density values for the tungsten - hard-metal composites were generally good except for the tungsten - hafnium boride, which had an unusually low density, particularly when its excellent stress-rupture properties are considered.

Hardness

While the diamond-pyramid-hardness values (table III, p. 16) for the extruded unreinforced tungsten ran from 360 to 383, the values for tungsten with oxide additives ran from 371 to 578, the hardness increasing with volume percent oxide.

With composites of tungsten - 8 to 10 volume percent oxide, the tungsten-hafnia composite gave a higher hardness than either the tungsten-zirconia or tungsten-yttria composites. With composites containing 14.5 to 25.5 volume percent oxides, the tungsten-zirconia approached the tungsten-hafnia composites in hardness, and both were significantly harder than the tungsten-yttria composite. The hardest material was obtained with the Curtiss-Wright hafnia - reinforced-tungsten composite.
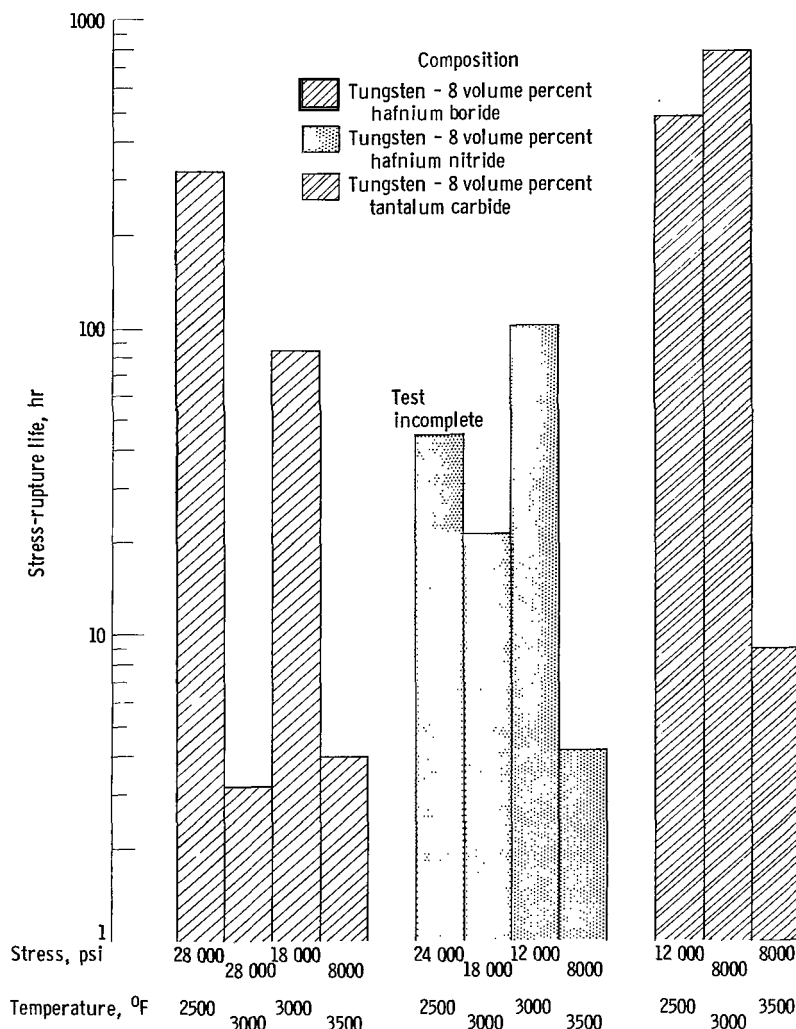
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Figure 11. - Stress-rupture tests of tungsten - 8-percent-refractory-compound composites at temperatures of 2500°, 3000°, and 3500° F.

The tungsten - hard-metal composites showed a large variation in hardness, ranging from the tungsten - tantalum carbide (diamond pyramid hardness, 315), which was lower than the unreinforced tungsten, to the tungsten - hafnium nitride, which was considerably higher (543).

Wide differences were noted in many cases between the cross-sectional and longitudinal hardness despite the fact that in a number of these cases the grain diameters were equal in both directions.

Grain Size

Grain diameter for unreinforced tungsten with an extrusion ratio of 8:1 ranged from 0.0028 to 0.0047 centimeter (see table III, p. 16). With additives, the grain diameter of the tungsten was considerably reduced and ranged from
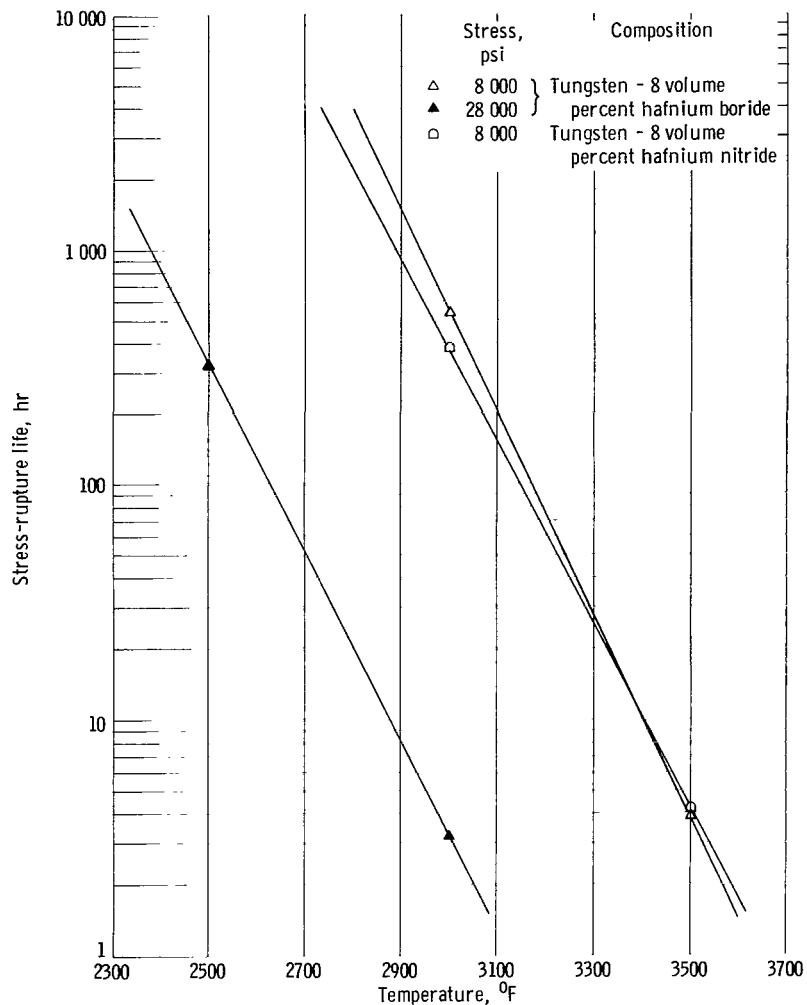
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Figure 12. - Effect of temperature on stress-rupture life of tungsten - refractory-compound composites.

0.0006 to 0.0030 centimeter. With 5 to 8 volume percent zirconia, the grain diameter ran from 0.0016 to 0.0023 centimeter, while with 14.5 to 25.5 volume percent zirconia, the grain size ran from 0.0009 to 0.0014 centimeter. The smallest grain size with oxides was obtained with the Curtiss-Wright tungsten-hafnia billet, 0.0005 to 0.0007 centimeter.

Grain sizes for the tungsten - hard-metal composites were quite variable, and considerable difference in the transverse and longitudinal grain size was found in the billets of tungsten - hafnium boride and tungsten - tantalum carbide. The smallest grain size with hard metals was obtained with hafnium nitride, 0.0006 to 0.0007 centimeter.

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DISCUSSION

Fibering

A new type of fiber product has been created by using powder metallurgy methods. Several oxide and refractory compounds have been successfully fibered (or elongated) in situ (in a tungsten matrix) by an extrusion process. The materials significantly fibered (L/D >10) were yttria, hafnium nitride, zirconia, and hafnia. The L/D values of the fibers in these composites ranged from 12.7 to 23.3. Additives that were fibered to a lesser extent included tantalum carbide, hafnium carbide, and thoria, with L/D values ranging from 5.1 to 7.8. With hafnium boride, fibering was observed only in the more highly deformed edges of the extrusion bar.

All materials with less than 10 volume percent additive that were significantly fibered had strengths greater than the unreinforced matrix. Unusually good stress-rupture properties were obtained with the hafnium nitride specimen. Its strength (i.e., creep resistance and stress-rupture life at 3000° F and 8000 psi and above) exceeded the strength of many of the better tungsten alloys (refs. 1 and 2). For comparison, the stress-rupture strength of one of the best tungsten alloys for which data are available is plotted in figure 10.

Since composites processed by the method described herein produced fibered products, it was not possible to prepare a control with an equiaxed structure in an equivalent manner, and therefore, the extent to which the fibering contributed to the increased strength could not be determined from this study.

Of the highly fibered products that were strengthened to a lesser extent than was the hafnium nitride bearing product, the strength increases were also significant and the stress-rupture lives were comparable with many tungsten alloys. In addition, the in situ fibering itself was of great interest. The fact that it has been demonstrated that fiber products can be made from an initially equiaxed powder is in itself important. Even in cases where additives are available in fiber form these fibers could be embedded in a metallic matrix and further elongated by processes directly comparable with those utilized in this investigation.

Reactions

The second objective of the investigation was to observe and to study reactions between tungsten and refractory additives. It was noted earlier that reactions might occur between refractory metals and refractory compounds and that these could have important effects on composite strengths. In the case of fiber-metal composites, for example, reactions between compounds and the matrix could affect the strength of the bond between the matrix and the additive, which in turn could affect the gross strength of the composites. Severe reactions could also damage the fiber or the matrix (ref. 9). The addition of refractory compounds, including oxides, carbides, nitrides, and so forth, in the form of small dispersoids to refractory matrices could also affect the

strength of composites because of reactions, as well as by dispersion strengthening. The mechanism by which dispersion-strengthened products are damaged is dissolution of an oxide or a compound and subsequent agglomeration of these products in other nucleation sites (ref. 10). Another type of possible reaction would be one in which the refractory compounds would react with the matrix and form other compounds. In some cases these might liquate and form relatively brittle networks. Much is yet to be learned about such relations in tungsten-base systems. Since these types of reactions can be important, it is most interesting to consider some of the results of the present paper.

Reactions were noted to occur in the composites where the additives elongated to a small extent only. In these specimens it is believed that the reactions enhanced the strength of the composites and that the strengthening resulting from the reactions was greater than the strength due to the fibering itself. The strengthening effects in such products are considered to be caused by separate strengthening mechanisms. For example, in one specimen taken from the nose of the tungsten - 8-volume-percent tantalum carbide extrusion bar there was evidence that the tantalum carbide that was fibered or tended to be fibered during processing was dissolved into the matrix and subsequently reprecipitated. It is not known, however, at which stage of the entire process precipitation occurred. Photomicrographs of the tungsten - tantalum carbide are shown in figures 13(a) to (c). These show the changes in microstructure, from front to back, of a single stress-rupture specimen machined from the nose of the extruded bar. It may be observed that both spheroids and a Widmanstätten type of precipitate are evident in the test area of the specimen (fig. 13(b)). Two electron micrographs (figs. 13(d) and (e)) show the middle areas of the specimen at a much higher magnification. Upstream from the nose, the tantalum carbide particles were relatively intact (see fig. 2(d)), and only a very small amount of carbide apparently had dissolved in the matrix. A specimen from this material, typical of the remainder of the bar, was not as good in stress-rupture at 3000° F as the specimen taken from the nose portion. The nose specimen had a creep rate three times as low as specimens taken from the rest of the bar. The reason for the greater reactions and the strength of the nose specimen is not known at this time.

The hafnium boride addition exhibited a completely different type of reaction with the matrix. The absence of fibering in the less deformed nose and middle of the bar may be due in part to the fact that the hafnium boride reacted with the tungsten to form a network of several phases. This reaction seemed to be one in which major transformations took place, including possibly some liquefaction, starting early in the sintering stage. The final microstructure consisted essentially of rounded tungsten rings, partially surrounded by a network of other phases, possibly tungsten boride (W_2B), a nonstoichiometric hafnium boride (Hf_xB_y), or a tungsten-hafnium intermetallic compound (fig. 2(a)). Even with this network structure, however, the material extruded readily, and in the creep-rupture test, exhibited relatively good elongation (8 percent) and an unusually high strength (see figs. 8 and 9). The presence of the tungsten boride (W_2B) phase was verified by X-ray analysis.

In the case of the specimens containing hafnium carbide it was observed that there were two types of phases embedded in the tungsten matrix
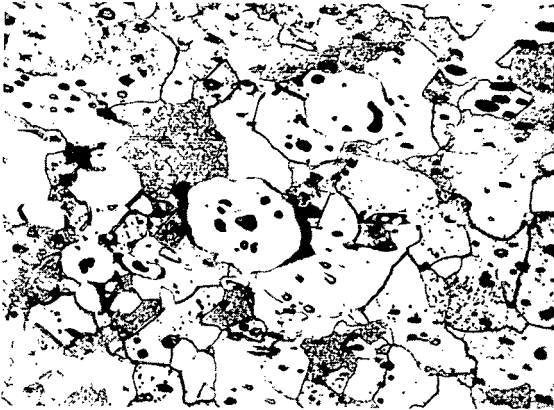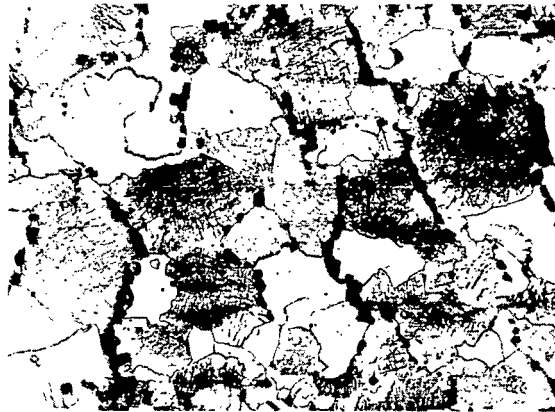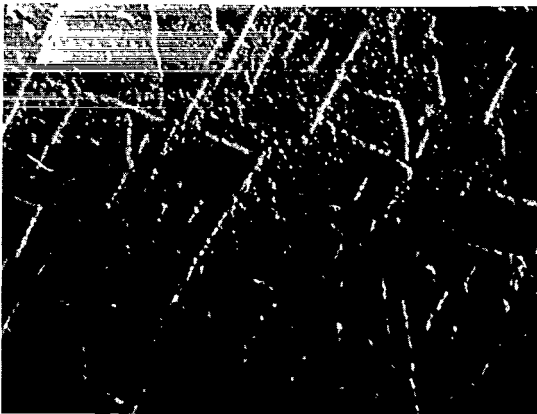
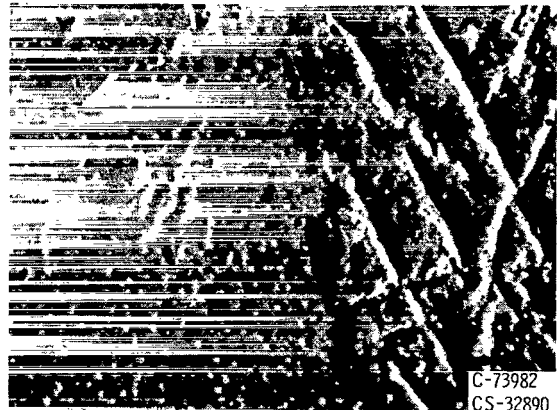(a) Front.
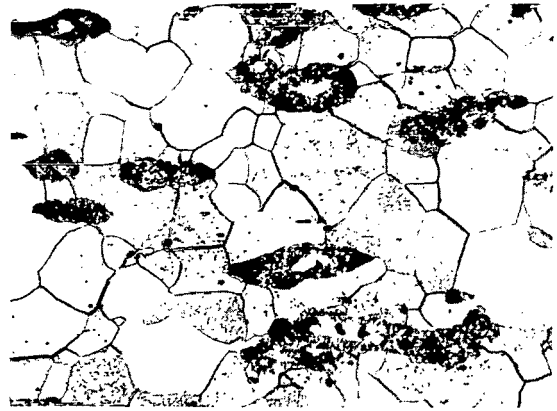
(c) Back.

(b) Test section.

Electron micrographs, X31 800

(d) Test section area 1.

(e) Test section area 2.

Figure 13. – Microstructures of stress-rupture specimen from nose of tungsten – tantalum carbide extrusion bar. (Reduced 30 percent in printing.)

(fig. 2(c), longitudinal section of nose of bar). A light gray phase (presumably hafnium carbide) was present in relatively large amounts. This phase was brittle and elongated only a small amount. The second phase, which was present in smaller concentration, was dark gray, ductile, and elongated to a greater degree. It is difficult to determine, in this case, if the strength of the tungsten was due to reactions with the hafnium carbide, because the strength of the composite increased very markedly without appreciable fibering or marked microstructural changes. The strength of this composite, as seen from figure 9, is very good. The strength is quite remarkable in view of the cracks in the microstructure. It is conceivable that the strength could be further increased if the structure could be made intact. Thus, in all cases discussed here, tungsten - tantalum carbide (nose and middle of bar), tungsten - hafnium boride, and tungsten - hafnium carbide, where the evidence for possible reaction is most prevalent, the strengths of the composites are very high and compare favorably with those of some of the best tungsten alloys and dispersion-strengthened materials discussed in the literature (refs. 1, 3, and 8). Figure 10 gives comparisons of the higher strength composites studied here and one of the better alloys in the literature.

A number of other considerations are of significance in the strengthening effects noted here. The addition of ceramic or refractory compounds to metallic matrices and the subsequent strengthening of the product usually presumes that the refractory compound is stable in the matrix to which it is added. If a fibered ceramic reacted with the matrix, it would not be expected to have the strength that it would have if it were completely inert, as it is imbedded in the material (ref. 9). Similarly, a dispersoid that dissolves into the matrix could be considered unstable, and, in fact, this solutioning of dispersoids in normal alloying processes is the usual strength limitation of most alloys. On the other hand, it appears that benefits may accrue to the developer of refractory-base materials because of reactions. For example, if a highly refractory and a highly stable compound with a high negative free energy of formation can be dissolved in the matrix and reprecipitated at a lower temperature, then the refractory material behaves as an alloy, and presumably, the structure could be heat treated in a manner similar to the way conventional alloys are heat treated. It certainly is well known that carbides readily dissolve in refractory metals. For example, in the case of molybdenum-base materials, the carbides in alloys of molybdenum, titanium, zirconium, and carbon are readily taken into solution and precipitated into different microstructures ranging from spheroids to Widmanstätten structures (ref. 11). Such microstructural changes are also common in many superalloys in lower melting point base materials. It is also well known that an oxide such as zirconia will form in a matrix of columbium and may be subsequently precipitated out in various microstructural configurations (ref. 12). This, too, permits the heat treating of a system containing a metal, a refractory, or a reactive material and an oxide ion to form a stable precipitate of an oxide. Some of these types of reactions were observed in this study.

Processing and General Observations

Another area of interest is the experience gained in the handling and

processing of tungsten-base systems. For example, it was shown that, by using a low-temperature hydrogen presintering prior to high-temperature vacuum sintering with tungsten, an increase in stress-rupture life and ductility was obtained. The improvement could have been due to decreasing the impurity content of the sintered compacts (ref. 13).

It has also been noted that the additives markedly affect the pressures required for extrusion. It may be postulated that oxides decrease the extrusion pressure required for tungsten because they are more easily deformed than the matrix at the extrusion temperature. In any event, oxide additions can be used to assist in processing tungsten.

Also, in view of the fact that the additives are lower in density than the tungsten, they all help to decrease the weight of the final product. Since they simultaneously strengthen the product, the combined effect markedly increases the strength-weight ratio. In the case of the oxides, it was noted that the strengthening effects were limited to oxide concentrations between 8 and 15 volume percent, since agglomeration and machining difficulties precluded obtaining a sufficient quantity of reliable specimens of the composites of higher volume percent oxide. This limitation may be overcome by better processing and machining techniques, or by using other types of additives. Normally, in a fiber-strengthened product it is anticipated that the strength will increase with increasing fiber content, possibly as high as 50 to 80 percent fiber. Thus, more substantial gains in strength-weight ratio with high concentrations of low-density fibers may yet be achieved in tungsten and other high-density matrices with the in situ fibering method.

It is quite evident from the density results that the bulk of the billets produced had good density, and this is confirmed by the fact that very little if any porosity can be seen in most of the microstructures. The reliability and reproducibility of density determinations by mercury displacement is generally good; thus, the slightly high and slightly low results obtained can only be partly attributed to the method employed. It is interesting to note that both high and low results were obtained with composites in which it was suspected reactions were occurring during the processing. Thus, if in a high-volume-percent-oxide composite some of the oxide were reduced to the higher density metal, or reacted to form a nonstoichiometric, oxygen-deficient higher density oxide, the theoretical density would increase and a determination based on the original composition would be high. With a tungsten - refractory-compound composite the tungsten additive reactions would tend to form lower density compounds such as tungsten boride (W_2B), and the theoretical density would be decreased. Then calculations based on the original composition would tend to be low, as observed with the tungsten - hafnium boride composite.

CONCLUDING REMARKS

The results of this investigation indicate that in situ fibering of refractory additives and controlled reactions between the additive and the matrix have good potential for producing strong materials for high-temperature applications.

In the preparation of fibered composites the in situ method offers several distinct advantages. First, since the additive is fibered within the metal, it is less subject to damage than if exposed to air or atmospheres with reactive impurities and to the rough handling and high pressures and temperatures required by the processing when fibers are embedded in a matrix in a conventional manner. Second, since the fiber surfaces are created in contact with the matrix during extrusion, the in situ process offers a better opportunity to obtain good bonding at the fiber-matrix interface. Third, in the in situ process, the matrix acts during the extrusion to distribute the stresses more nearly isostatically around the additive particles, and this permits relatively strong, hard, and brittle additives to be deformed and elongated. Thus, the advantages inherent in the in situ process will permit the reinforcement of composites with materials not yet available in fiber form and with other materials from which fibers may not readily be made in any other manner.

The criteria for determining the optimum properties for a fiber-composite matrix material have not been fully established; however, it is generally agreed that, in order to utilize the full strength of the composite, the elongation of the matrix should be greater than that of the fibers so that the load is shifted to and shared with the fibers. It is therefore conceivable that strong useful fiber composites could be obtained by applying the in situ method to other matrix materials such as tantalum and columbium, which have lower moduli and higher creep rates than tungsten. For the purposes of this study, the high melting point of tungsten offered the use of a wide range of temperature required for processing and a relatively stiff matrix, which could better transmit to the less deformable additives the high stresses necessary to elongate them during extrusion. In addition, it was desired to note any reactions between tungsten and the additives because of the implications these could have in other fields of interest, such as dispersion strengthening.

Most of the products in which reactions were observed exhibited high-strength properties at elevated temperatures. The reactions between the compounds and the tungsten, however, indicated possible difficulties associated with the creation of dispersion-strengthened tungsten alloys in that such materials might have an upper use temperature that depends on the nature of the reactions that occur. Even the most thermodynamically stable additives may react with tungsten in a manner analogous to that observed here as the temperature approaches the melting point of the matrix or the additive. Nevertheless, the results suggest that products with high strength at high temperatures can be made from high-melting-point materials containing refractory compounds by controlling the reactions between the compounds and the matrix by heat treatments.

SUMMARY OF RESULTS

An investigation conducted to demonstrate the feasibility of producing fibers in situ (in the matrix of high-temperature materials) during extrusion, and to study reactions between refractory additives and a tungsten matrix with a view toward producing high-strength tungsten-base materials has produced the following results:

1. Four oxides (zirconia, yttria, hafnia, and thoria) and four refractory compounds (hafnium boride, hafnium carbide, hafnium nitride, and tantalum carbide) were elongated or fibered in situ (in a tungsten matrix) by extrusion. Despite a wide range in the melting points of the additives, 4370° to 7030° F, some fibering was obtained in all cases. In general, the oxide additives (length-diameter ratios of 7.8 to 23.3) were elongated more effectively than the refractory compounds (length-diameter ratios of 1.0 to 18.4).

2. Several tungsten-plus-additive specimens with good stress-rupture strength and creep resistance were obtained from the tungsten - refractory-compound billets. The strength appeared to be the result of reactions or alloying between the additives and the matrix rather than the fibering itself. The refractory-compound additives increased the stress-rupture life of the tungsten composites 25 to 50 times. The results obtained exceeded most of the stress-rupture properties noted in the literature for tungsten-base materials.

3. The stress-rupture lives of the tungsten composites containing 8 to 10 volume percent additives with the most highly elongated fibers (zirconia, yittria, hafnia, and hafnium nitride) ranged from 4 to 18 times better than that of the unreinforced matrix; however, it was not possible to determine from this study how much of the improvement was due to fibering.

4. With tungsten-thoria composites, a small increase in stress-rupture life was obtained on increasing the concentration of thoria from 8 to 16 volume percent, while with the other oxide additives, a maximum stress-rupture life was obtained at 8 to 10 volume percent. The decrease in stress-rupture life with higher oxide concentrations may be attributed to the oxide agglomeration and machining difficulties observed in these billets.

5. Double sintering using first hydrogen and then a vacuum improved the strength properties of unreinforced tungsten relative to a single vacuum sintering. Very little effect on stress-rupture life could be noted due to other processing variables such as canning, extrusion ratio, and use of the high-energy press as compared with the conventional extrusion press.

6. The extrusion pressure required for the composites, as compared with tungsten, generally decreased with the addition of oxides and increased with the addition of refractory compounds.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, February 1, 1965.

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